

## PATENT ABSTRACTS OF JAPAN

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## (54) PROPYLENE-ETHYLENE COPOLYMER AND ITS PRODUCTION

(57)Abstract:

PURPOSE: To provide a propylene-ethylene copolymer excellent in flexibility, clarity, and heat resistance.

CONSTITUTION: A propylene-ethylene copolymer has a wt. average mol.wt. of 100,000-1,500,000, contains 5-60mol% ethylene units, and comprises 1-60wt.% polypropylene blocks having an intrinsic viscosity  $[\eta]$  of 7dl/g or higher and a xylene-sol. content at room temp. of 0.5wt.% or lower and 40-99wt.% propylene-ethylene random copolymer blocks having an intrinsic viscosity of 0.5-7dl/g and a xylene-sol. content at room temp. of 50wt.% or higher.

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**CLAIMS**

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**[Claim(s)]**

[Claim 1] It is a block copolymer containing polypropylene component 1 - 60wt% and propylene ethylene random-copolymer component 40 - 99wt%. Limiting viscosity  $[\eta]$  is [ the component of fusibility of a polypropylene component ] less than [ 5wt% ] at 7 or more dl/g and the xylene in a room temperature. Limiting viscosity  $[\eta]$  a propylene ethylene random-copolymer component 0.5 - 7 dl/g, and the monomeric unit further based on [ the component of the xylene fusibility in a room temperature is more than 50wt%, and ] ethylene -- 5-60-mol% -- the propylene ethylene copolymer which contains and is characterized by the weight average molecular weight of the whole copolymer being 100,000-1,500,000.

[Claim 2] Under existence of the catalyst which consists of the following component (A) titanium compound (B) organoaluminium compound and the (C) electron donor It is made to generate. first, the polypropylene whose component of fusibility the polymerization of a propylene is performed in a first stage polymerization, and limiting viscosity  $[\eta]$  is less than [ 5wt% ] at 7 or more dl/g and the xylene in a room temperature -- 1 - 60wt% of all laps -- subsequently Copolymerization of a propylene and ethylene is performed in a second stage polymerization. Limiting viscosity  $[\eta]$  0.5 - 7 dl/g, And the component of the xylene fusibility in a room temperature is more than 50wt%. the monomeric unit based on ethylene -- 5-60-mol% -- the included propylene ethylene random copolymer -- 40 - 99wt% of all laps -- the manufacture approach of the propylene ethylene copolymer according to claim 1 characterized by making it generate.

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DETAILED DESCRIPTION

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[Detailed Description of the Invention]

[0001]

[Industrial Application] This invention relates to the propylene ethylene copolymer excellent in thermal resistance, shock resistance, and transparency.

[0002]

[Description of the Prior Art] Since thermoplastic elastomer olefin has the outstanding flexibility and has high weatherability by low specific gravity, it begins autoparts, such as a bumper, and is broadly used for various industrial components, household-electric-appliances components, etc. As these thermoplastic elastomer olefin, in order to satisfy the shock resistance in low temperature, and flexibility, generally melting kneading of ethylene propylene rubber (EPR) or ethylene-propylene terpolymer (EPDM), and the polypropylene resin is carried out, and it is manufactured by the approach of constructing a bridge before kneading or over the back partially by the case. such an approach -- for example, JP,47-18943,A -- said -- 48-26838 -- said -- 49-53938 -- said -- it is indicated by 54-1386. Moreover, the approach of raising thermal resistance is indicated in JP,61-264043,A, JP,2-140236,A, and JP,59-30736,B, without spoiling flexibility by carrying out dynamic bridge formation of the blend objects, such as a constituent which added the diolefin to the copolymer obtained by the three-step polymerization which consists of a propylene with which ethylene contents differ, and ethylene, and the propylene ethylene copolymer, PP, EPDM, EPR, and a divinylbenzene, respectively. However, this approach manufactures each polymer beforehand, and in order that productivity may be bad and may construct a bridge from subsequently blending, transparency cannot use for the application of a film, a sheet, etc. bad, but has the problem that it is difficult to recycle further.

[0003] On the other hand, in order to solve these problems, a multistage polymerization method is used, and the approach of carrying out the polymerization of each component within the same polymerization tank gradually is proposed. for example, JP,55-80418,A -- said -- although 57-10611 was mentioned, flexibility and thermal resistance were inadequate. Since it was forced a temperature change with it while the Provisional-Publication-No. 57-61012 official report of amelioration of a hauling property is inadequate, stable production was difficult from the problem of cooling. [ low and polymerization temperature and ] [ large ] moreover, JP,58-145718,A -- and -- said -- 58-71910 was insufficient as an object which maintained balance about each physical properties, although the approach to have improved thermal resistance, shock resistance, and transparency by the three-step polymerization from which the presentation which consists of a propylene, ethylene, and a 1-butene differs was indicated. Thus, what is depended on a direct polymerization method had flexibility, transparency, and the problem that thermal resistance and oilproof were missing, although further excelled also in the cost and recycle nature on manufacture.

[0004] As mentioned above, flexibility and transparency were good and, moreover, development of heat-resistant good thermoplastic elastomer olefin was desired.

[0005]

[Means for Solving the Problem] Header this invention was completed for the propylene ethylene block copolymer which consists of a propylene ethylene copolymer component which has the

polypropylene component and the specific viscosity which have specific viscosity as a result of inquiring wholeheartedly being the elastomer in which flexibility and transparency have good and high thermal resistance that this invention persons should solve the above-mentioned technical problem. .

[0006] Namely, this invention is a block copolymer containing polypropylene component 1 - 60wt% and propylene ethylene random-copolymer component 40 - 99wt%. Limiting viscosity [eta] is [ the component of fusibility of a polypropylene component ] less than [ 5wt% ] at 7 or more dl/g and the xylene in a room temperature. Limiting viscosity [eta] a propylene ethylene random-copolymer component 0.5 - 7 dl/g, and the monomeric unit further based on [ the component of the xylene fusibility in a room temperature is more than 50wt%, and ] ethylene -- 5-60-mol% -- it is the propylene ethylene copolymer which contains and is characterized by the weight average molecular weight of the whole copolymer being 100,000-1,500,000.

[0007] The percentage of occupying in [ all ] a polymer needs to be 1 - 60wt%, and the polypropylene component in the propylene ethylene copolymer of this invention is 3 - 40wt% preferably. moreover, the monomeric unit based on ethylene in a propylene ethylene random-copolymer component (only henceforth a random-copolymer component) -- 5-60-mol% -- desirable -- 8-50-mol% -- the rate of containing and occupying the amount in [ all ] a polymer - 40 - 99wt% -- it is necessary to be 60 - 99wt% preferably When a polypropylene component exceeds 60wt(s)%, or when the monomeric unit based on the ethylene in a random-copolymer component is less than [ 5mol% ], the property as polypropylene becomes strong and sufficient flexibility and the outstanding shock resistance are no longer demonstrated. On the other hand, when the monomeric unit based on the ethylene in a random-copolymer component exceeds 60-mol%, the property as polyethylene becomes strong, and since \*\*\*\* impact strength and thermal resistance become less enough, it is not desirable.

[0008] Limiting viscosity [eta] must be 7 or more dl/g, and the polypropylene component in the propylene ethylene copolymer of this invention is 9 - 25 dl/g preferably. In the ethylene presentation which limiting viscosity [eta] described above in less than 7 dl/g, the heat-resistant improvement effectiveness falls and is not desirable. Moreover, limiting viscosity [eta] must be 0.5 - 7 dl/g, and the random-copolymer component of the propylene ethylene copolymer of this invention has the desirable range of 1.0 - 5 dl/g. Since limiting viscosity becomes less enough [ less than 0.5 dl/g / thermal resistance and shock resistance ] as, it is not desirable. In addition, the limiting viscosity in this invention is the value measured at 135 degrees C by using a tetralin as a solvent.

[0009] Moreover, to the xylene in a room temperature, the component of fusibility needs to be less than [ 5wt% ], and further 0.1 - 3wt% of the polypropylene component in the propylene ethylene copolymer of this invention is desirable. This is because it is [ that the molecular weight of a polypropylene component is very large as mentioned above, and ] a crystalline high polypropylene component as mentioned later. Therefore, if the component of xylene fusibility exceeds 5wt(s)%, in order to maintain the thermal resistance of a propylene ethylene copolymer on predetermined level, it is necessary to raise the rate of occupying in all the polymers of a polypropylene component, or to lower the ethylene content in a random copolymer, and the shock resistance of all copolymers will fall as a result. On the other hand, the component of the xylene fusibility in the room temperature in a random-copolymer component needs to be more than 50wt%, and is desirable. [ further 60 - 100wt% of ] This becomes [ crystallinity ] high that the component of the xylene fusibility which is because a random-copolymer component needs to have amorphism nature or the elastomer-property of very low crystallinity is less than [ 50wt% ] too much and is not desirable.

[0010] Weight average molecular weight (it omits Following Mw) is 100,000-1,500,000, and when the molecular weight of a propylene ethylene copolymer takes a moldability into consideration, its range of 200,000-1 million is more desirable. Since a moldability will turn up and the target physical properties will no longer be acquired if Mw crosses the aforementioned range, it is not desirable. Moreover, as for the molecular weight distribution (Mw/Mn) of the propylene ethylene copolymer of this invention, it is desirable that it is the range of 3-15. In addition, the weight average molecular weight in this invention was measured with gel permeation chromatography (it

abbreviates to GPC hereafter). Although the propylene ethylene copolymer of this invention may be obtained by what kind of approach, especially the following approach is adopted preferably. [0011] Under existence of the catalyst which consists of the following component (A) titanium compound (B) organoaluminium compound and the (C) electron donor It is made to generate. first, the polypropylene whose component of fusibility the polymerization of a propylene is performed in a first stage polymerization, and limiting viscosity  $[\eta]$  is less than  $[5\text{wt}\%]$  at 7 or more dl/g and the xylene in a room temperature -- 1 - 60wt% of all laps -- subsequently Copolymerization of a propylene and ethylene is performed in a second stage polymerization. Limiting viscosity  $[\eta]$  0.5 - 7 dl/g, and the monomeric unit based on [ the component of the xylene fusibility in a room temperature is more than 50wt%, and ] ethylene -- 5-60-mol% -- the included propylene ethylene random copolymer -- 40 - 99wt% of all laps -- it is obtained by making it generate.

[0012] the well-known titanium compound and well-known organoaluminium compound with which the titanium compound which is the (A) component of this invention is used for the polymerization of an olefin -- what -- it is used without grade limits. As a titanium compound, alpha, beta, gamma, or delta-3 titanium chloride can be used. Especially, for example JP,47-34478,A, said -- 50-126590 -- said -- 50-114394 -- said -- 50-93888 -- said -- 50-12309 -- said -- 50-74594 -- said -- 50-104191 -- said -- 50-98489 -- said -- 51-136625 -- said -- 52-30888 -- said -- by the approach indicated by each official report of 52-35283 it was prepared -- high -- an activity titanium compound is used suitably.

[0013] moreover, the titanium compound supported by support, such as a magnesium chloride, - - \*\*\*\* for suitable -- things are made. For example, JP,56-155206,A, said -- 56-136806 -- said -- 57-34103 -- said -- 58-8706 -- said -- 58-83006 -- said -- 58-138708 -- said -- 58-183709 -- said -- 59-206408 -- said -- 59-219311 -- said -- 60-1208 -- said -- 60-81209 -- said -- 60-186508 -- said -- 60-192708 -- said -- 61-211309 -- said -- 61-271304 -- said -- 62-15209 -- said -- 62-11706 -- said -- by the approach shown in 62-72702 and this 62-104810 grade The titanium compound supported by support, such as a prepared magnesium chloride, is used.

[0014] The organoaluminium compound which is the (B) component of this invention is used that what is generally used for the polymerization of an olefin combining a titanium compound does not have a limit in any way. For example, alkylaluminum, such as alkylaluminum hydrides, such as trialkylaluminums, such as halogenation alkylaluminum, such as a diethylaluminium chloride, ethylaluminium sesquichloride, and ethyl aluminum dichloride, triethylaluminum, and triisobutylaluminum, and a diethyl aluminum hydride, and alkyl aluminoxane, can be illustrated, and these organoaluminium compounds are independent or can be used combining two or more kinds.

[0015] In this invention, it is desirable to perform precuring of an olefin to the bottom of existence of an above-mentioned titanium compound and an above-mentioned organoaluminium compound. As for the amount of the organoaluminium compound used in precuring, the range of 0.1-20 is preferably adopted as 0.01-100, and a pan by aluminum/Ti (mole ratio) to the titanium atom of a titanium compound.

[0016] A propylene, ethylene, 1-butene, 1-pentene, 1-hexene, 1-octene, a 3-methyl-1-butene, 4-methyl-1-pentene, etc. are mentioned, and the olefin used by precuring can be independent, or can mix these, and can be used.

[0017] Moreover, the approach of carrying out precuring of congener or the olefin of a different kind to a multistage story is also employable. As for the lap of the above-mentioned olefin, it is desirable that they are per 1g of titanium compounds and 0.1-100g, and it is desirable to a pan that it is the range of 0.5-50g.

[0018] As for precuring, it is desirable to usually apply solution polymerization, and it is independent in hydrocarbons, such as a hexane, a heptane, a cyclohexane, and toluene, as a solvent, or can mix and use it.

[0019] An electron donor may be added in case precuring is performed. The electron donor used can use the well-known compound used for the polymerization of an olefin that there is no limit in any way. Specifically, the ether, an amine, an amide, ester, a sulfur compound, phosphorus

compounds, a nitril compound, a carboxylic acid, an organic silicon compound, and a halogenated compound are mentioned.

[0020] Unless the effectiveness of this invention is spoiled, the conditions of others in precuring, for example, temperature, a pressure, and time amount are not limited, but you may decide on them suitably. It is desirable to wash the generated titanium content polyolefine after precuring termination using the above-mentioned hydrocarbon solvent.

[0021] This polymerization is performed after the above-mentioned precuring. In this polymerization, the polymerization of a propylene is performed in a first stage polymerization, and, subsequently random copolymerization of a propylene and ethylene is performed in the 2nd-step polymerization. In the polymerization of the propylene of a first stage story, although an organoaluminium compound is added, even when this is the same as that of the organoaluminium compound used at the time of precuring, different species are also available for it. The amount of the organoaluminium compound used has the desirable range of 1-500 to 1-5000, and a pan to the titanium atom of a titanium compound at aluminum/Ti (mole ratio).

[0022] What is necessary is for the polymerization percentage of a propylene to be 1 - 60wt%, and just to determine it suitably according to the physical properties of the propylene ethylene copolymer made into the purpose to all laps. Namely, what is necessary is to be so desirable that there be few laps of a propylene when you need flexibility and transparency, and just to make it increase a lap, when you need high intensity and the object of a high degree of hardness more.

[0023] Generally polymerization temperature has [ the polymerization conditions of a propylene ] the desirable range of 40-80 degrees C 0-100 degrees C. Any, such as a slurry polymerization which uses the propylene itself as a solvent, a vapor phase polymerization, and solution polymerization, are sufficient as a polymerization, further, a polymerization is divided into two or more steps where conditions differ, and it can also perform it.

[0024] In the polymerization of a propylene, in order to raise the stereoregularity of the polymer to generate, the electron donor which is the (C) component can be added. The well-known electron donor of the electron donor to be used used for the polymerization of the conventional olefin is [ that there is no limit in any way ] usable. Specifically A methanol, ethanol, propanol, a butanol, Alcohols, such as a pentanol and a hexanol; A phenol, cresol, Phenols, such as a xylenol; An acetone, a methyl ethyl ketone, methyl isobutyl ketone, Ketones, such as a cyclohexanone and an acetophenone; An acetaldehyde, Aldehydes, such as propionaldehyde and a benzaldehyde; Methyl acetate, Ethyl acetate, vinyl acetate, methyl propionate, ethyl propionate, Methyl butyrate, ethyl butylate, ethyl valerianate, stearin acid ethyl, an ethyl acrylate, Organic-acid ester, such as a methyl methacrylate, ethyl benzoate, and ethyl phthalate; An ethyl silicate, Silicate ester, such as dicyclopenthyll dimetoxysilane and phenyltriethoxysilane Ether, such as ethyl ether, isopropyl ether, a tetrahydrofuran, and an anisole; The acetic amide, amides [ , such as a benzoic-acid amide, ]; -- nitril [ , such as amines; acetonitriles, such as 2,2,6,6-tetramethylpiperidine and 2,4,6-trimethylpyridine, and a benzonitrile, ]; -- in addition to this, a sulfur-containing electron donor; phosphorus-containing electron donor can be mentioned. Silicate ester [ , such as organic-acid ester; methyl isobutyl ketone, / , such as ketones; dicyclopenthyll dimetoxysilane, ], such as a methyl methacrylate and butyl acetate, is used suitably especially.

[0025] Although what is necessary is for the additions of hydrogen to be the polymerization rate of a polypropylene component, and balance with the limiting viscosity of polypropylene to generate, and just to determine them suitably in consideration of the physical properties of the propylene ethylene copolymer made into the purpose, as for hydrogen, not adding is desirable in order to heighten effectiveness more.

[0026] Next, random copolymerization of the propylene which is the 2nd-step polymerization, and ethylene is performed to the bottom of existence of the electron donor which are a molecular weight modifier, an organoaluminium compound, and the (C) component. Although a well-known thing is used as a molecular weight modifier that there is no limit in any way, the hydrogen used the general-purpose is desirable.

[0027] Although the organoaluminium compound was described above, an others and alkylaluminum alkoxide can be suitably used for it. Specifically A dimethyl aluminum methoxide,

dimethyl aluminum ethoxide, A diethyl aluminum methoxide, diethyl aluminum ethoxide, Diethyl aluminum n-butoxide, diethyl aluminum isobutoxide, Diethyl aluminum t-butoxide, diethyl aluminum oct KISHIDO, A diethyl aluminum phenoxide, ethyl aluminum sesquiethoxide, Ethyl aluminum NIUMUJI ethoxide, ethyl aluminum chloride MONOETOKISHIDO, Ethyl aluminum BUROMAIDOMONO ethoxide, a diethyl aluminum phenoxide, Diethyl aluminum (2, 6-dimethyl phenoxide), diethyl aluminum (2, 6-diisobutyl phenoxide), Diethyl aluminum (2, 6-G t-butyl phenoxide), diethyl aluminum (2, 6-diphenyl phenoxide), Ethyl aluminum NIUMUJI (2, 6-G t-butyl phenoxide), ethyl aluminum NIUMUJI (2, 6-G t-butyl-4-methyl phenoxide), etc. can be mentioned.

[0028] Moreover, the electron donor used in the 2nd-step polymerization of this invention can use the same thing as the electron donor used in the 1st-step polymerization mentioned above.

[0029] the organoaluminium compound with which the organoaluminium compound used the addition of the organoaluminium compound used by the 2nd-step polymerization, and an electron donor by the 1st-step polymerization -- receiving -- 0.01-10 -- further -- the organoaluminium compound with which 0.1-1 (mole ratio) are desirable with an organoaluminium compound, and an electron donor is used by the 2nd-step polymerization on the other hand -- receiving -- 0.001-10 -- further -- the range of 0.001-1 (mole ratio) is desirable.

[0030] What is necessary is for the polymerization percentage of a random-copolymer component to be 40 - 99wt%, and just to determine it suitably according to the physical properties of the propylene ethylene copolymer made into the purpose to all laps.

[0031] Although any, such as a vapor phase polymerization, a slurry polymerization, and solution polymerization, are sufficient as the random copolymerization of a propylene and ethylene, since the amount of the residual aluminum in a rate of polymerization and the copolymer obtained can be lessened, the slurry polymerization which uses the propylene itself as a solvent is used preferably. In this case, in order to dilute a catalyst component in addition to a propylene solvent, a small amount of inert hydrocarbon may be contained.

[0032] In the random copolymerization of a propylene and ethylene, although hydrogen is made to live together as a molecular-weight modifier, the limiting viscosity [ $\eta$ ] of the copolymer obtained should just determine suitably that a propylene, ethylene, and the gaseous-phase gas concentration of hydrogen will become 0.5 - 7 dl/g in 97.5/2/0.5-42.5/42.5/15 (mole ratio) so that the propylene of a copolymer and the presentation of ethylene which are acquired may become 40-95-mol% and 5-60-mol%, respectively. As for polymerization temperature, the range of 0-100 degrees C and further 40-80 degrees C is adopted preferably. Moreover, after performing the approach, for example, a polymerization with a low ethylene presentation in the preceding paragraph, of dividing a polymerization into two or more steps where conditions differ, and performing it, the approach of changing hydrogen concentration in the method of performing a polymerization with an ethylene presentation high in the latter part and the preceding paragraph, and the latter part etc. is employable. You may decide on polymerization time amount suitably from polymerization temperature and a lap. The propylene ethylene copolymer obtained by this invention can be used as the mold goods which have various configurations by various kinds of fabricating methods, such as injection molding, extrusion molding, and press forming, without performing decomposition by the peroxide.

[0033]

[Effect] According to this invention, heat-resistant good thermoplastic elastomer olefin can be obtained, without spoiling flexibility and transparency. Moreover, in order not to perform the decomposition process by the peroxide, the odor originating in decomposition survival etc. is lost, and the copolymer of high quality can be manufactured.

[0034]

[Example] Hereafter, although an example and the example of a comparison are given and this invention is explained, this invention is not limited to these examples.

[0035] In addition, the physical-properties value in an example is measured by the following approach.

[0036] Limiting viscosity (it abbreviates to [ $\eta$ ] below): It measured at 135 degrees C with the tetralin solvent.

[0037] [eta] P ... The limiting viscosity of the polymer generated in the 1st step is shown.

[0038] [eta] EP ... The limiting viscosity of the polymer which carried out the polymerization in the 2nd step is shown.

[0039] [eta] T ... The limiting viscosity of all polymers is shown.

[0040] [eta] EP is the value computed by the following approach.

[0041]

[Formula 1]

$$[\eta]_{EP} = \frac{[\eta]_T - [\eta]_P(P)}{(EP)}$$

(P) : : 第1段階の重合割合  
(EP) : : 第2段階の重合割合

[0042] Room-temperature xylene extractives: After having carried out the temperature up to 135 degrees C, and also having continued stirring for 30 minutes, making it dissolve completely and considering as a uniform solution, having added polymer 1g to 100ml of para xylene, and stirring it, it cooled to the room temperature and was left at the room temperature for further 24 hours. After carrying out a \*\* exception by suction filtration, the weight of the polymer which was made to carry out evaporation to dryness of the filtrate, and remained was found.

[0043] Weight average molecular weight: Using Waters GPC-150C, o-dichlorobenzene was used as the solvent and it measured at 135 degrees C. The used column is Showa Denko SHODEX. It is UT806L.

[0044] Ethylene content: The ethylene content was measured using the infrared absorption spectrum.

[0045] Bending elastic modulus: Create a 12.7mmx12.7mmx3.1mm test piece with a Japan Steel Works J120SAII mold injection molding machine, and it is JIS. It carried out according to K7203.

[0046] BIKATTO softening temperature: Use the test piece for bending elastic-modulus measurement, and it is JIS. It carried out according to K7206.

[0047] Degree of hardness: JIS The test piece was created according to K7215, and it measured using A mold testing machine.

[0048] Izod impactive strength: JIS It measured according to K7110.

[0049] Internal Hayes: The T die was attached in the extruder after corning the mixture which added the antioxidant and the thermostabilizer to the polymer, the sheet with a thickness of 0.5mm was fabricated with the melting resin temperature of 230 degrees C, and the test piece was prepared. After applying a liquid paraffin to both sides of this test piece, Hayes was measured according to JISK7150 and transparency was evaluated.

[0050] After nitrogen gas fully permuted the glass autoclave reactor of 1l. of content volume equipped with example 1 (precuring) agitator, hexane 400ml was put in. Subsequently, diethylaluminium chloride 14.5mmol, diethylene-glycol JIMETOKISHIDO 0.18mmol, and ethyl-iodide 18.1mmol were added, and whenever [ reactor internal temperature ] was kept at 15 degrees C. After adding titanium-trichloride (Marubeni Solvay chemistry company make) 18.1mmol, the propylene was continuously introduced into the reactor for 30 minutes so that it might be set to 3g per 1g of catalysts. After suspending supply of a propylene, as a result of nitrogen gas's permuting the inside of a reactor enough and analyzing the obtained titanium content polypropylene, the polymerization of the 2.9g [ per 1g of catalysts ] propylene was carried out. Then, 1-butene was continuously introduced into the reactor for 90 minutes so that it might be set to 10g per 1g of catalysts. In addition, temperature in the meantime was held at 15 degrees C. After suspending supply of 1-butene, nitrogen gas permuted the inside of a reactor enough, and the obtained titanium content Pori (propylene-1-butene) copolymer was washed 5 times by the purification hexane. The 14.6g [ per 1g of catalysts ] polymer was generating as a result of analysis.

[0051] (This polymerization) After nitrogen gas fully permuted the autoclave reactor made from stainless steel of 2l. of content volume equipped with the agitator, 1l. and a diethylaluminium chloride were added for the liquid propylene 1.1 mmols, and the temperature up of the inside of a reactor was carried out to 55 degrees C. 0.14mmol(s) were added to the bottom of nitrogen-

gas-atmosphere method by making into a titanium trichloride the titanium content polymer obtained by precuring. After performing homopolymerization of a propylene for 30 minutes at 55 degrees C, diethyl aluminum sesquithoxide 0.33mmol and methyl-methacrylate 0.055mmol were added, installation of hydrogen and ethylene was started successfully, and ethylene gas concentration supplied so that seven-mol % and hydrogen gas concentration might become two-mol%, and performed the polymerization of a propylene and ethylene for 120 minutes at 55 degrees C. After removing an unreacted propylene, ethylene, and hydrogen after polymerization termination, the propylene ethylene copolymer was obtained by processing with propylene oxide and water. A result is shown in Table 1 and 2.

[0052] The same actuation as an example 1 was performed except having replaced with the conditions which showed the addition of the ethylene concentration in the polymerization temperature of two to example 9 example 1, polymerization time amount, and a gaseous phase, hydrogen concentration and an alkylaluminum alkoxide, or an electron donor in Table 1. A result is shown in Table 1 and 2.

[0053] Preparation of an example 10 (preparation of titanium component) titanium component was performed according to the approach of the example 1 of JP,58-83006,A. The obtained solid-state titanium compound was magnesium 18.0wt% and diisobutyl phthalate 21.9wt% chlorine 57.0wt% titanium 2.1wt% as a result of analysis.

[0054] (Precuring) After nitrogen gas fully permuted the glass autoclave reactor of 1l. of content volume equipped with the agitator, hexane 400ml was put in. Whenever [ reactor internal temperature ] was kept at 15 degrees C, and triethylaluminum 50mmol, diphenyldimethoxysilane 10mmol, ethyl-iodide 50mmol, and a solid-state titanium catalyst component were added 5 mmols by titanium atom conversion. The propylene was continuously introduced into the reactor for 1 hour so that it might be set to 3g per 1g of catalysts. After suspending supply of a propylene, as a result of nitrogen gas's permuting the inside of a reactor enough and analyzing the obtained titanium content polypropylene, the polymerization of the 3.0g [ per 1g of catalysts ] propylene was carried out.

[0055] (This polymerization) After having added 1l., triethylaluminum 0.5mmol, and diphenyldimethoxysilane 0.5mmol for the liquid propylene after nitrogen gas fully permuted the autoclave reactor made from stainless steel of 2l. of content volume equipped with the stirrer, and carrying out the temperature up of the inside of a reactor to 55 degrees C, 0.002mmol(s) were added for the titanium content polymer obtained by precuring to the bottom of nitrogen-gas-atmosphere method by titanium atom conversion. After performing homopolymerization of a propylene for 30 minutes at 55 degrees C, installation of hydrogen and ethylene was started successfully, and ethylene gas concentration supplied so that seven-mol % and hydrogen gas concentration might become two-mol%, and performed the polymerization of a propylene and ethylene for 120 minutes at 55 degrees C. After removing an unreacted propylene, ethylene, and hydrogen after polymerization termination, the propylene ethylene copolymer was obtained by processing with propylene oxide and water. A result is shown in Table 1 and 2.

[0056] In example of comparison 1 example 1, the same actuation as an example 1 was performed except having not added hydrogen at the time of the random copolymerization of propylene ethylene. 1, 3-screw (t-butyl PAOKI seesaw propyl) benzene, the antioxidant, and the thermostabilizer were added, it corned and injection molding was carried out to the obtained polymer. A result is shown in Table 1 and 2.

[0057] Organic peroxide was not added, but the antioxidant and the thermostabilizer were added, it corned and injection molding was carried out to the polymer which carried out the polymerization like the example 1 of example of comparison 2 comparison. A result is shown in Table 1 and 2.

[0058] Injection molding was corned and carried out, after carrying out separate manufacture of the example 3 of a comparison, 4 polypropylene components, and the random-copolymer component, respectively and adding and carrying out the dryblend of an anti-oxidant and the thermostabilizer to the obtained polymer. In addition, what was decomposed using the peroxide which used the polymer obtained by performing only the 2nd-step polymerization in the example 1 in the example 1 of a comparison was used for the random-copolymer component. the example

3 of a comparison -- a polypropylene component -- the example 4 of 5wt(s)% and a comparison -- a polypropylene component -- 20wt(s)% -- it added. A result is shown in Table 2.

[0059] Injection molding was carried out after carrying out the dryblend of the random-copolymer component obtained by performing only the 2nd-step polymerization of a polypropylene component and an example 1 obtained by carrying out the polymerization only of the 1st-step polymerization of the example 5 of a comparison, and six examples 1 at hydrogen concentration % of two mols. A result is shown in Table 2.

[0060] In example of comparison 7 example 1, it carried out by the same approach as an example 1 except having added hydrogen and having performed the polymerization at the time of the 1st-step polymerization. The antioxidant and the thermostabilizer were added, it carried out injection molding was carried out to the obtained polymer. A result is shown in Table 1 and 2.

[0061]

[Table 1]

表 1

	プロピレン重合			プロピレンエチレン共重合						重合活性 (g/g-Cat)
	温度 (°C)	時間 (min)	水素濃度 (mol%)	Et <sub>2</sub> Al <sub>2</sub> (OEt) <sub>2</sub> (mmol)	タタリ酸 (mmol)	温度 (°C)	時間 (min)	水素濃度 (mol%)	エチレン濃度 (mol%)	
実施例 1	55	30	0	0.33	0.055	55	120	2.0	7	6500
2	55	30	0	0.33	0.055	55	120	0.5	7	6300
3	55	30	0	0.33	0.055	55	120	4.0	7	7500
4	70	60	0	0.33	0.11	55	90	2.0	13	6900
5	70	60	0	0.33	0.11	55	90	5.0	13	8800
6	55	30	0	0.33	0.055	55	120	2.0	3	5400
7	55	30	0	0.33	0.055	55	120	2.0	2	4900
8	70	120	0	0.33	0.11	55	90	4.0	15	8300
9	70	180	0	0.33	0.11	55	80	4.0	15	8800
10	55	30	0	-	-	55	120	2.0	7	24000
比較例 1、2	55	30	0	0.33	0.055	55	120	0	7	5500
7	55	30	2.0	0.33	0.055	55	120	2.0	7	7200

[0062]

[Table 2]

表 2

	ポリプロピレン成分			ランダム共重合成分						プロピレンエチレン共重合体						
	$[\eta]$ <sub>r</sub> (dl/g)	P-sol <sup>1)</sup> (wt%)	(P) <sup>2)</sup> (wt%)	$[\eta]$ <sub>EP</sub> (dl/g)	P-sol <sup>1)</sup> (wt%)	エチン含有量 (mol%)	$[\eta]$ <sub>r</sub> (dl/g)	$M_w$ ( $\times 10^{-4}$ )	$M_w/M_n$	曲げ弾性率 (Kg/cm <sup>2</sup> )	軟化温度 (°C)	Izod衝撃強 度(-30°C)	硬度	$\Delta T_g$ (°C)		
実施例 1	11.8	1.0	7	4.0	81	22.5	4.5	77	12	1450	110	NB	91	15		
2	11.8	1.0	7	5.2	80	21.5	5.5	85	11	1500	115	NB	92	16		
3	11.8	1.0	6	3.7	88	23.4	4.2	73	12	1300	108	NB	91	15		
4	13.2	0.9	19	4.6	90	34.6	6.2	88	12	1100	109	NB	83	41		
5	13.2	0.9	15	4.1	93	35.3	5.5	82	13	1000	106	NB	83	39		
6	11.8	1.0	8	2.5	75	12.0	3.2	58	11	1700	128	NB	92	16		
7	11.8	1.0	9	2.3	71	8.2	3.2	55	11	2300	140	NB	95	17		
8	12.9	0.9	22	4.1	94	39.8	6.0	85	13	1700	130	NB	92	88		
9	12.9	0.9	29	4.0	96	57.6	6.6	88	15	3100	158	NB	96	89		
10	9.6	0.9	8	3.2	85	19.8	3.4	61	7	1100	108	NB	85	19		
比較例 1	11.8	1.0	8	22.6	75	22.8	2.2 <sup>3)</sup>	34	3	1050	93	NB	84	18		
2	11.8	1.0	8	22.6	75	22.8	2.4 <sup>4)</sup>	26	4	980	81	NB	80	18		
3	11.8	1.0	5	2.2	93	22.6	2.7	28	4	1300	99	NB	88	25		
4	11.8	1.0	20	2.2	93	22.6	4.1	73	6	2500	132	NB	95	38		
5	3.8	6.8	5	22.6	75	22.6	2.6 <sup>4)</sup>	26	5	1450	88	NB	90	18		
6	3.8	6.8	20	22.6	75	22.6	2.6 <sup>4)</sup>	26	6	2600	111	NB	95	24		
7	3.8	6.8	14	4.2	80	22.7	4.1	54	13	1100	91	NB	83	20		

1)室温でのp-キシシレン可溶成分量  
2)ポリプロピレン成分の重合割合  
3)分解後の極限粘度  
4)成形後の極限粘度

1)室温でのp-キシレン可溶成分量      2)ポリプロピレン成分の重合割合      3)分解後の極限粘度      4)成形後の極限粘度

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TECHNICAL FIELD

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[Industrial Application] This invention relates to the propylene ethylene copolymer excellent in thermal resistance, shock resistance, and transparency.

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EFFECT OF THE INVENTION

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[Effect] According to this invention, heat-resistant good thermoplastic elastomer olefin can be obtained, without spoiling flexibility and transparency. Moreover, in order not to perform the decomposition process by the peroxide, the odor originating in decomposition survival etc. is lost, and the copolymer of high quality can be manufactured.

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## TECHNICAL PROBLEM

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[Description of the Prior Art] Since thermoplastic elastomer olefin has the outstanding flexibility and has high weatherability by low specific gravity, it begins autoparts, such as a bumper, and is broadly used for various industrial components, household-electric-appliances components, etc. As these thermoplastic elastomer olefin, in order to satisfy the shock resistance in low temperature, and flexibility, generally melting kneading of ethylene propylene rubber (EPR) or ethylene-propylene terpolymer (EPDM), and the polypropylene resin is carried out, and it is manufactured by the approach of constructing a bridge before kneading or over the back partially by the case. such an approach -- for example, JP,47-18943,A -- said -- 48-26838 -- said -- 49-53938 -- said -- it is indicated by 54-1386. Moreover, the approach of raising thermal resistance is indicated in JP,61-264043,A, JP,2-140236,A, and JP,59-30736,B, without spoiling flexibility by carrying out dynamic bridge formation of the blend objects, such as a constituent which added the diolefin to the copolymer obtained by the three-step polymerization which consists of a propylene with which ethylene contents differ, and ethylene, and the propylene ethylene copolymer, PP, EPDM, EPR, and a divinylbenzene, respectively. However, this approach manufactures each polymer beforehand, and in order that productivity may be bad and may construct a bridge from subsequently blending, transparency cannot use for the application of a film, a sheet, etc. bad, but has the problem that it is difficult to recycle further.

[0003] On the other hand, in order to solve these problems, a multistage polymerization method is used, and the approach of carrying out the polymerization of each component within the same polymerization tank gradually is proposed. for example, JP,55-80418,A -- said -- although 57-10611 was mentioned, flexibility and thermal resistance were inadequate. Since it was forced a temperature change with it while the Provisional-Publication-No. 57-61012 official report of amelioration of a hauling property is inadequate, stable production was difficult from the problem of cooling. [ low and polymerization temperature and ] [ large ] moreover, JP,58-145718,A -- and -- said -- 58-71910 was insufficient as an object which maintained balance about each physical properties, although the approach to have improved thermal resistance, shock resistance, and transparency by the three-step polymerization from which the presentation which consists of a propylene, ethylene, and a 1-butene differs was indicated. Thus, what is depended on a direct polymerization method had flexibility, transparency, and the problem that thermal resistance and oilproof were missing, although further excelled also in the cost and recycle nature on manufacture.

[0004] As mentioned above, flexibility and transparency were good and, moreover, development of heat-resistant good thermoplastic elastomer olefin was desired.

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MEANS

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[Means for Solving the Problem] Header this invention was completed for the propylene ethylene block copolymer which consists of a propylene ethylene copolymer component which has the polypropylene component and the specific viscosity which have specific viscosity as a result of inquiring wholeheartedly being the elastomer in which flexibility and transparency have good and high thermal resistance that this invention persons should solve the above-mentioned technical problem. .

[0006] Namely, this invention is a block copolymer containing polypropylene component 1 - 60wt% and propylene ethylene random-copolymer component 40 - 99wt%. Limiting viscosity [eta] is [ the component of fusibility of a polypropylene component ] less than [ 5wt% ] at 7 or more dl/g and the xylene in a room temperature. Limiting viscosity [eta] a propylene ethylene random-copolymer component 0.5 - 7 dl/g, and the monomeric unit further based on [ the component of the xylene fusibility in a room temperature is more than 50wt%, and ] ethylene -- 5-60-mol% -- it is the propylene ethylene copolymer which contains and is characterized by the weight average molecular weight of the whole copolymer being 100,000-1,500,000.

[0007] The percentage of occupying in [ all ] a polymer needs to be 1 - 60wt%, and the polypropylene component in the propylene ethylene copolymer of this invention is 3 - 40wt% preferably. moreover, the monomeric unit based on ethylene in a propylene ethylene random-copolymer component (only henceforth a random-copolymer component) -- 5-60-mol% -- desirable -- 8-50-mol% -- the rate of containing and occupying the amount in [ all ] a polymer - 40 - 99wt% -- it is necessary to be 60 - 99wt% preferably When a polypropylene component exceeds 60wt(s)%, or when the monomeric unit based on the ethylene in a random-copolymer component is less than [ 5mol% ], the property as polypropylene becomes strong and sufficient flexibility and the outstanding shock resistance are no longer demonstrated. On the other hand, when the monomeric unit based on the ethylene in a random-copolymer component exceeds 60-mol%, the property as polyethylene becomes strong, and since \*\*\*\* impact strength and thermal resistance become less enough, it is not desirable.

[0008] Limiting viscosity [eta] must be 7 or more dl/g, and the polypropylene component in the propylene ethylene copolymer of this invention is 9 - 25 dl/g preferably. In the ethylene presentation which limiting viscosity [eta] described above in less than 7 dl/g, the heat-resistant improvement effectiveness falls and is not desirable. Moreover, limiting viscosity [eta] must be 0.5 - 7 dl/g, and the random-copolymer component of the propylene ethylene copolymer of this invention has the desirable range of 1.0 - 5 dl/g. Since limiting viscosity becomes less enough [ less than 0.5 dl/g / thermal resistance and shock resistance ] as, it is not desirable. In addition, the limiting viscosity in this invention is the value measured at 135 degrees C by using a tetralin as a solvent.

[0009] Moreover, to the xylene in a room temperature, the component of fusibility needs to be less than [ 5wt% ], and further 0.1 - 3wt% of the polypropylene component in the propylene ethylene copolymer of this invention is desirable. This is because it is [ that the molecular weight of a polypropylene component is very large as mentioned above, and ] a crystalline high polypropylene component as mentioned later. Therefore, if the component of xylene fusibility exceeds 5wt(s)%, in order to maintain the thermal resistance of a propylene ethylene copolymer

on predetermined level, it is necessary to raise the rate of occupying in all the polymers of a polypropylene component, or to lower the ethylene content in a random copolymer, and the shock resistance of all copolymers will fall as a result. On the other hand, the component of the xylene fusibility in the room temperature in a random-copolymer component needs to be more than 50wt%, and is desirable. [ further 60 - 100wt% of ] This becomes [ crystallinity ] high that the component of the xylene fusibility which is because a random-copolymer component needs to have amorphism nature or the elastomer-property of very low crystallinity is less than [ 50wt% ] too much and is not desirable.

[0010] Weight average molecular weight (it omits Following Mw) is 100,000-1,500,000, and when the molecular weight of a propylene ethylene copolymer takes a moldability into consideration, its range of 200,000-1 million is more desirable. Since a moldability will turn up and the target physical properties will no longer be acquired if Mw crosses the aforementioned range, it is not desirable. Moreover, as for the molecular weight distribution (Mw/Mn) of the propylene ethylene copolymer of this invention, it is desirable that it is the range of 3-15. In addition, the weight average molecular weight in this invention was measured with gel permeation chromatography (it abbreviates to GPC hereafter). Although the propylene ethylene copolymer of this invention may be obtained by what kind of approach, especially the following approach is adopted preferably.

[0011] Under existence of the catalyst which consists of the following component (A) titanium compound (B) organoaluminium compound and the (C) electron donor It is made to generate. first, the polypropylene whose component of fusibility the polymerization of a propylene is performed in a first stage polymerization, and limiting viscosity [eta] is less than [ 5wt% ] at 7 or more dl/g and the xylene in a room temperature -- 1 - 60wt% of all laps -- subsequently Copolymerization of a propylene and ethylene is performed in a second stage polymerization. Limiting viscosity [eta] 0.5 - 7 dl/g, and the monomeric unit based on [ the component of the xylene fusibility in a room temperature is more than 50wt%, and ] ethylene -- 5-60-mol% -- the included propylene ethylene random copolymer -- 40 - 99wt% of all laps -- it is obtained by making it generate.

[0012] the well-known titanium compound and well-known organoaluminium compound with which the titanium compound which is the (A) component of this invention is used for the polymerization of an olefin -- what -- it is used without grade limits. As a titanium compound, alpha, beta, gamma, or delta-3 titanium chloride can be used. Especially, for example JP,47-34478,A, said -- 50-126590 -- said -- 50-114394 -- said -- 50-93888 -- said -- 50-12309 -- said -- 50-74594 -- said -- 50-104191 -- said -- 50-98489 -- said -- 51-136625 -- said -- 52-30888 -- said -- by the approach indicated by each official report of 52-35283 it was prepared -- high -- an activity titanium compound is used suitably.

[0013] moreover, the titanium compound supported by support, such as a magnesium chloride, - - \*\*\*\* for suitable -- things are made. For example, JP,56-155206,A, said -- 56-136806 -- said -- 57-34103 -- said -- 58-8706 -- said -- 58-83006 -- said -- 58-138708 -- said -- 58-183709 -- said -- 59-206408 -- said -- 59-219311 -- said -- 60-1208 -- said -- 60-81209 -- said -- 60-186508 -- said -- 60-192708 -- said -- 61-211309 -- said -- 61-271304 -- said -- 62-15209 -- said -- 62-11706 -- said -- by the approach shown in 62-72702 and this 62-104810 grade The titanium compound supported by support, such as a prepared magnesium chloride, is used.

[0014] The organoaluminium compound which is the (B) component of this invention is used that what is generally used for the polymerization of an olefin combining a titanium compound does not have a limit in any way. For example, alkylaluminum, such as alkylaluminum hydrides, such as trialkylaluminums, such as halogenation alkylaluminum, such as a diethylaluminium chloride, ethylaluminium sesquichloride, and ethyl aluminum dichloride, triethylaluminum, and triisobutylaluminum, and a diethyl aluminum hydride, and alkyl aluminoxane, can be illustrated, and these organoaluminium compounds are independent or can be used combining two or more kinds.

[0015] In this invention, it is desirable to perform precuring of an olefin to the bottom of existence of an above-mentioned titanium compound and an above-mentioned organoaluminium compound. As for the amount of the organoaluminium compound used in precuring, the range of

0.1-20 is preferably adopted as 0.01-100, and a pan by aluminum/Ti (mole ratio) to the titanium atom of a titanium compound.

[0016] A propylene, ethylene, 1-butene, 1-pentene, 1-hexene, 1-octene, a 3-methyl-1-butene, 4-methyl-1-pentene, etc. are mentioned, and the olefin used by precuring can be independent, or can mix these, and can be used.

[0017] Moreover, the approach of carrying out precuring of congener or the olefin of a different kind to a multistage story is also employable. As for the lap of the above-mentioned olefin, it is desirable that they are per 1g of titanium compounds and 0.1-100g, and it is desirable to a pan that it is the range of 0.5-50g.

[0018] As for precuring, it is desirable to usually apply solution polymerization, and it is independent in hydrocarbons, such as a hexane, a heptane, a cyclohexane, and toluene, as a solvent, or can mix and use it.

[0019] An electron donor may be added in case precuring is performed. The electron donor used can use the well-known compound used for the polymerization of an olefin that there is no limit in any way. Specifically, the ether, an amine, an amide, ester, a sulfur compound, phosphorus compounds, a nitril compound, a carboxylic acid, an organic silicon compound, and a halogenated compound are mentioned.

[0020] Unless the effectiveness of this invention is spoiled, the conditions of others in precuring, for example, temperature, a pressure, and time amount are not limited, but you may decide on them suitably. It is desirable to wash the generated titanium content polyolefine after precuring termination using the above-mentioned hydrocarbon solvent.

[0021] This polymerization is performed after the above-mentioned precuring. In this polymerization, the polymerization of a propylene is performed in a first stage polymerization, and, subsequently random copolymerization of a propylene and ethylene is performed in the 2nd-step polymerization. In the polymerization of the propylene of a first stage story, although an organoaluminium compound is added, even when this is the same as that of the organoaluminium compound used at the time of precuring, different species are also available for it. The amount of the organoaluminium compound used has the desirable range of 1-500 to 1-5000, and a pan to the titanium atom of a titanium compound at aluminum/Ti (mole ratio).

[0022] What is necessary is for the polymerization percentage of a propylene to be 1 - 60wt%, and just to determine it suitably according to the physical properties of the propylene ethylene copolymer made into the purpose to all laps. Namely, what is necessary is to be so desirable that there be few laps of a propylene when you need flexibility and transparency, and just to make it increase a lap, when you need high intensity and the object of a high degree of hardness more.

[0023] Generally polymerization temperature has [ the polymerization conditions of a propylene ] the desirable range of 40-80 degrees C 0-100 degrees C. Any, such as a slurry polymerization which uses the propylene itself as a solvent, a vapor phase polymerization, and solution polymerization, are sufficient as a polymerization, further, a polymerization is divided into two or more steps where conditions differ, and it can also perform it.

[0024] In the polymerization of a propylene, in order to raise the stereoregularity of the polymer to generate, the electron donor which is the (C) component can be added. The well-known electron donor of the electron donor to be used used for the polymerization of the conventional olefin is [ that there is no limit in any way ] usable. Specifically A methanol, ethanol, propanol, a butanol, Alcohols, such as a pentanol and a hexanol; A phenol, cresol, Phenols, such as a xylenol; An acetone, a methyl ethyl ketone, methyl isobutyl ketone, Ketones, such as a cyclohexanone and an acetophenone; An acetaldehyde, Aldehydes, such as propionaldehyde and a benzaldehyde; Methyl acetate, Ethyl acetate, vinyl acetate, methyl propionate, ethyl propionate, Methyl butyrate, ethyl butylate, ethyl valerianate, stearin acid ethyl, an ethyl acrylate, Organic-acid ester, such as a methyl methacrylate, ethyl benzoate, and ethyl phthalate; An ethyl silicate, Silicate ester, such as dicyclopenthyll dimetoxysilane and phenyltriethoxysilane Ether, such as ethyl ether, isopropyl ether, a tetrahydrofuran, and an anisole; The acetic amide, amides [ , such as a benzoic-acid amide, ]; -- nitril [ , such as amines; acetonitriles, such as 2,2,6,6-tetramethylpiperidine and 2,4,6-trimethylpyridine, and a benzonitrile, ]; -- in addition to this, a sulfur-containing electron donor; phosphorus-containing electron donor can be mentioned.

Silicate ester [, such as organic-acid ester; methyl isobutyl ketone, /, such as ketones; dicyclopenthyll dimetoxysilane, ], such as a methyl methacrylate and butyl acetate, is used suitably especially.

[0025] Although what is necessary is for the additions of hydrogen to be the polymerization rate of a polypropylene component, and balance with the limiting viscosity of polypropylene to generate, and just to determine them suitably in consideration of the physical properties of the propylene ethylene copolymer made into the purpose, as for hydrogen, not adding is desirable in order to heighten effectiveness more.

[0026] Next, random copolymerization of the propylene which is the 2nd-step polymerization, and ethylene is performed to the bottom of existence of the electron donor which are a molecular weight modifier, an organoaluminium compound, and the (C) component. Although a well-known thing is used as a molecular weight modifier that there is no limit in any way, the hydrogen used the general-purpose is desirable.

[0027] Although the organoaluminium compound was described above, an others and alkylaluminum alkoxide can be suitably used for it. Specifically A dimethyl aluminum methoxide, dimethyl aluminum ethoxide, A diethyl aluminum methoxide, diethyl aluminum ethoxide, Diethyl aluminum n-butoxide, diethyl aluminum isobutoxide, Diethyl aluminum t-butoxide, diethyl aluminum oct KISHIDO, A diethyl aluminum phenoxide, ethyl aluminum sesquiethoxide, Ethyl aluminum NIUMUJI ethoxide, ethyl aluminum chloride MONOETOKISHIDO, Ethyl aluminum BUROMAIDOMONO ethoxide, a diethyl aluminum phenoxide, Diethyl aluminum (2, 6-dimethyl phenoxide), diethyl aluminum (2, 6-diisobutyl phenoxide), Diethyl aluminum (2, 6-G t-butyl phenoxide), diethyl aluminum (2, 6-diphenyl phenoxide), Ethyl aluminum NIUMUJI (2, 6-G t-butyl phenoxide), ethyl aluminum NIUMUJI (2, 6-G t-butyl-4-methyl phenoxide), etc. can be mentioned.

[0028] Moreover, the electron donor used in the 2nd-step polymerization of this invention can use the same thing as the electron donor used in the 1st-step polymerization mentioned above.

[0029] the organoaluminium compound with which the organoaluminium compound used the addition of the organoaluminium compound used by the 2nd-step polymerization, and an electron donor by the 1st-step polymerization -- receiving -- 0.01-10 -- further -- the organoaluminium compound with which 0.1-1 (mole ratio) are desirable with an organoaluminium compound, and an electron donor is used by the 2nd-step polymerization on the other hand -- receiving -- 0.001-10 -- further -- the range of 0.001-1 (mole ratio) is desirable.

[0030] What is necessary is for the polymerization percentage of a random-copolymer component to be 40 - 99wt%, and just to determine it suitably according to the physical properties of the propylene ethylene copolymer made into the purpose to all laps.

[0031] Although any, such as a vapor phase polymerization, a slurry polymerization, and solution polymerization, are sufficient as the random copolymerization of a propylene and ethylene, since the amount of the residual aluminum in a rate of polymerization and the copolymer obtained can be lessened, the slurry polymerization which uses the propylene itself as a solvent is used preferably. In this case, in order to dilute a catalyst component in addition to a propylene solvent, a small amount of inert hydrocarbon may be contained.

[0032] In the random copolymerization of a propylene and ethylene, although hydrogen is made to live together as a molecular-weight modifier, the limiting viscosity [ $\eta$ ] of the copolymer obtained should just determine suitably that a propylene, ethylene, and the gaseous-phase gas concentration of hydrogen will become 0.5 - 7 dl/g in 97.5/2/0.5-42.5/42.5/15 (mole ratio) so that the propylene of a copolymer and the presentation of ethylene which are acquired may become 40-95-mol% and 5-60-mol%, respectively. As for polymerization temperature, the range of 0-100 degrees C and further 40-80 degrees C is adopted preferably. Moreover, after performing the approach, for example, a polymerization with a low ethylene presentation in the preceding paragraph, of dividing a polymerization into two or more steps where conditions differ, and performing it, the approach of changing hydrogen concentration in the method of performing a polymerization with an ethylene presentation high in the latter part and the preceding paragraph, and the latter part etc. is employable. You may decide on polymerization time amount suitably from polymerization temperature and a lap. The propylene ethylene copolymer obtained

by this invention can be used as the mold goods which have various configurations by various kinds of fabricating methods, such as injection molding, extrusion molding, and press forming, without performing decomposition by the peroxide.

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## EXAMPLE

[Example] Hereafter, although an example and the example of a comparison are given and this invention is explained, this invention is not limited to these examples.

[0035] In addition, the physical-properties value in an example is measured by the following approach.

[0036] Limiting viscosity (it abbreviates to [eta] below): It measured at 135 degrees C with the tetralin solvent.

[0037] [eta] P ... The limiting viscosity of the polymer generated in the 1st step is shown.

[0038] [eta] EP ... The limiting viscosity of the polymer which carried out the polymerization in the 2nd step is shown.

[0039] [eta] T ... The limiting viscosity of all polymers is shown.

[0040] [eta] EP is the value computed by the following approach.

[0041]

[Formula 1]

$$[\eta]_{EP} = \frac{[\eta]_T - [\eta]_P (P)}{(EP)}$$

(P) : 第1段階の重合割合  
(EP) : 第2段階の重合割合

[0042] Room-temperature xylene extractives: After having carried out the temperature up to 135 degrees C, and also having continued stirring for 30 minutes, making it dissolve completely and considering as a uniform solution, having added polymer 1g to 100ml of para xylene, and stirring it, it cooled to the room temperature and was left at the room temperature for further 24 hours. After carrying out a \*\* exception by suction filtration, the weight of the polymer which was made to carry out evaporation to dryness of the filtrate, and remained was found.

[0043] Weight average molecular weight: Using Waters GPC-150C, o-dichlorobenzene was used as the solvent and it measured at 135 degrees C. The used column is Showa Denko SHODEX. It is UT806L.

[0044] Ethylene content: The ethylene content was measured using the infrared absorption spectrum.

[0045] Bending elastic modulus: Create a 12.7mmx12.7mmx3.1mm test piece with a Japan Steel Works J120SAII mold injection molding machine, and it is JIS. It carried out according to K7203.

[0046] BIKATTO softening temperature: Use the test piece for bending elastic-modulus measurement, and it is JIS. It carried out according to K7206.

[0047] Degree of hardness: JIS The test piece was created according to K7215, and it measured using A mold testing machine.

[0048] Izod impactive strength: JIS It measured according to K7110.

[0049] Internal Hayes: The T die was attached in the extruder after corning the mixture which added the antioxidant and the thermostabilizer to the polymer, the sheet with a thickness of 0.5mm was fabricated with the melting resin temperature of 230 degrees C, and the test piece was prepared. After applying a liquid paraffin to both sides of this test piece, Hayes was measured according to JISK7150 and transparency was evaluated.

[0050] After nitrogen gas fully permuted the glass autoclave reactor of 1l. of content volume

equipped with example 1 (precuring) agitator, hexane 400ml was put in. Subsequently, diethylaluminium chloride 14.5mmol, diethylene-glycol JIMETOKISHIDO 0.18mmol, and ethyl-iodide 18.1mmol were added, and whenever [ reactor internal temperature ] was kept at 15 degrees C. After adding titanium-trichloride (Marubeni Solvay chemistry company make) 18.1mmol, the propylene was continuously introduced into the reactor for 30 minutes so that it might be set to 3g per 1g of catalysts. After suspending supply of a propylene, as a result of nitrogen gas's permuting the inside of a reactor enough and analyzing the obtained titanium content polypropylene, the polymerization of the 2.9g [ per 1g of catalysts ] propylene was carried out. Then, 1-butene was continuously introduced into the reactor for 90 minutes so that it might be set to 10g per 1g of catalysts. In addition, temperature in the meantime was held at 15 degrees C. After suspending supply of 1-butene, nitrogen gas permuted the inside of a reactor enough, and the obtained titanium content Pori (propylene-1-butene) copolymer was washed 5 times by the purification hexane. The 14.6g [ per 1g of catalysts ] polymer was generating as a result of analysis.

[0051] (This polymerization) After nitrogen gas fully permuted the autoclave reactor made from stainless steel of 2l. of content volume equipped with the agitator, 1l. and a diethylaluminium chloride were added for the liquid propylene 1.1 mmols, and the temperature up of the inside of a reactor was carried out to 55 degrees C. 0.14mmol(s) were added to the bottom of nitrogen-gas-atmosphere mind by making into a titanium trichloride the titanium content polymer obtained by precuring. After performing homopolymerization of a propylene for 30 minutes at 55 degrees C, diethyl aluminum sesquioxides 0.33mmol and methyl-methacrylate 0.055mmol were added, installation of hydrogen and ethylene was started succeedingly, and ethylene gas concentration supplied so that seven-mol % and hydrogen gas concentration might become two-mol%, and performed the polymerization of a propylene and ethylene for 120 minutes at 55 degrees C. After removing an unreacted propylene, ethylene, and hydrogen after polymerization termination, the propylene ethylene copolymer was obtained by processing with propylene oxide and water. A result is shown in Table 1 and 2.

[0052] The same actuation as an example 1 was performed except having replaced with the conditions which showed the addition of the ethylene concentration in the polymerization temperature of two to example 9 example 1, polymerization time amount, and a gaseous phase, hydrogen concentration and an alkylaluminum alkoxide, or an electron donor in Table 1. A result is shown in Table 1 and 2.

[0053] Preparation of an example 10 (preparation of titanium component) titanium component was performed according to the approach of the example 1 of JP,58-83006,A. The obtained solid-state titanium compound was magnesium 18.0wt% and diisobutyl phthalate 21.9wt% chlorine 57.0wt% titanium 2.1wt% as a result of analysis.

[0054] (Precuring) After nitrogen gas fully permuted the glass autoclave reactor of 1l. of content volume equipped with the agitator, hexane 400ml was put in. Whenever [ reactor internal temperature ] was kept at 15 degrees C, and triethylaluminum 50mmol, diphenyldimethoxysilane 10mmol, ethyl-iodide 50mmol, and a solid-state titanium catalyst component were added 5 mmols by titanium atom conversion. The propylene was continuously introduced into the reactor for 1 hour so that it might be set to 3g per 1g of catalysts. After suspending supply of a propylene, as a result of nitrogen gas's permuting the inside of a reactor enough and analyzing the obtained titanium content polypropylene, the polymerization of the 3.0g [ per 1g of catalysts ] propylene was carried out.

[0055] (This polymerization) After having added 1l., triethylaluminum 0.5mmol, and diphenyldimethoxysilane 0.5mmol for the liquid propylene after nitrogen gas fully permuted the autoclave reactor made from stainless steel of 2l. of content volume equipped with the stirrer, and carrying out the temperature up of the inside of a reactor to 55 degrees C, 0.002mmol(s) were added for the titanium content polymer obtained by precuring to the bottom of nitrogen-gas-atmosphere mind by titanium atom conversion. After performing homopolymerization of a propylene for 30 minutes at 55 degrees C, installation of hydrogen and ethylene was started succeedingly, and ethylene gas concentration supplied so that seven-mol % and hydrogen gas concentration might become two-mol%, and performed the polymerization of a propylene and

ethylene for 120 minutes at 55 degrees C. After removing an unreacted propylene, ethylene, and hydrogen after polymerization termination, the propylene ethylene copolymer was obtained by processing with propylene oxide and water. A result is shown in Table 1 and 2.

[0056] In example of comparison 1 example 1, the same actuation as an example 1 was performed except having not added hydrogen at the time of the random copolymerization of propylene ethylene. 1, 3-screw (t-butyl PAOKI seesaw propyl) benzene, the antioxidant, and the thermostabilizer were added, it corned and injection molding was carried out to the obtained polymer. A result is shown in Table 1 and 2.

[0057] Organic peroxide was not added, but the antioxidant and the thermostabilizer were added, it corned and injection molding was carried out to the polymer which carried out the polymerization like the example 1 of example of comparison 2 comparison. A result is shown in Table 1 and 2.

[0058] Injection molding was corned and carried out, after carrying out separate manufacture of the example 3 of a comparison, 4 polypropylene components, and the random-copolymer component, respectively and adding and carrying out the dryblend of an anti-oxidant and the thermostabilizer to the obtained polymer. In addition, what was decomposed using the peroxide which used the polymer obtained by performing only the 2nd-step polymerization in the example 1 in the example 1 of a comparison was used for the random-copolymer component. the example 3 of a comparison -- a polypropylene component -- the example 4 of 5wt(s)% and a comparison -- a polypropylene component -- 20wt(s)% -- it added. A result is shown in Table 2.

[0059] Injection molding was corned and carried out after carrying out the dryblend of the random-copolymer component obtained by performing only the 2nd-step polymerization of a polypropylene component and an example 1 obtained by carrying out the polymerization only of the 1st-step polymerization of the example 5 of a comparison, and six examples 1 at hydrogen concentration % of two mols. A result is shown in Table 2.

[0060] In example of comparison 7 example 1, it carried out by the same approach as an example 1 except having added hydrogen and having performed the polymerization at the time of the 1st-step polymerization. The antioxidant and the thermostabilizer were added, it corned and injection molding was carried out to the obtained polymer. A result is shown in Table 1 and 2.

[0061]

[Table 1]

表 1

	プロピレン重合			プロピレンエチレン共重合						重合活性 (g/g-Cat)
	温度 (°C)	時間 (min)	水素濃度 (mol%)	Et <sub>2</sub> Al <sub>2</sub> (OEt) <sub>2</sub> (mmol)	イタリル酸ジナ (mmol)	温度 (°C)	時間 (min)	水素濃度 (mol%)	イタリル濃度 (mol%)	
実施例 1	55	30	0	0.33	0.055	55	120	2.0	7	6500
2	55	30	0	0.33	0.055	55	120	0.5	7	6300
3	55	30	0	0.33	0.055	55	120	4.0	7	7500
4	70	60	0	0.33	0.11	55	90	2.0	13	6900
5	70	60	0	0.33	0.11	55	90	5.0	13	8800
6	55	30	0	0.33	0.055	55	120	2.0	3	5400
7	55	30	0	0.33	0.055	55	120	2.0	2	4900
8	70	120	0	0.33	0.11	55	90	4.0	15	8300
9	70	180	0	0.33	0.11	55	80	4.0	15	8800
10	55	30	0	-	-	55	120	2.0	7	24000
比較例 1、2	55	30	0	0.33	0.055	55	120	0	7	5500
7	55	30	2.0	0.33	0.055	55	120	2.0	7	7200

[0062]

[Table 2]

表 2

	ポリプロピレン成分			ランダム共重合成分				プロピレンエチレン共重合体						
	[ $\eta$ ] <sub>r</sub> (dl/g)	P-sol <sup>1)</sup> (wt%)	(P) <sup>2)</sup> (wt%)	[ $\eta$ ] <sub>sp</sub> (dl/g)	P-sol <sup>1)</sup> (wt%)	1/2含有量 (mol%)	[ $\eta$ ] <sub>r</sub> (dl/g)	M <sub>w</sub> ( $\times 10^4$ )	M <sub>w</sub> /M <sub>n</sub>	曲げ弾性率 (Kg/cm <sup>2</sup> )	軟化温度 (°C)	120d衝撃強 度(-30°C)	硬度	$\Delta T_g$ (°C)
実施例 1	11.8	1.0	7	4.0	81	22.5	4.5	77	12	1450	110	NB	91	15
2	11.8	1.0	7	5.2	80	21.5	5.5	85	11	1500	115	NB	92	16
3	11.8	1.0	6	3.7	88	23.4	4.2	73	12	1300	108	NB	91	15
4	13.2	0.9	19	4.6	90	94.6	6.2	88	12	1100	109	NB	83	41
5	13.2	0.9	15	4.1	93	35.3	5.5	82	13	1000	106	NB	83	39
6	11.8	1.0	8	2.5	75	12.0	3.2	58	11	1700	128	NB	92	16
7	11.8	1.0	9	2.3	71	8.2	3.2	55	11	2300	140	NB	95	17
8	12.9	0.9	22	4.1	94	39.8	6.0	85	13	1700	130	NB	92	88
9	12.9	0.9	29	4.0	96	57.6	6.6	88	15	3100	158	NB	96	89
10	9.6	0.9	8	3.2	85	19.8	3.4	61	7	1100	108	NB	85	19
比較例 1	11.8	1.0	8	22.6	75	22.8	2.2 <sup>3)</sup>	34	3	1050	93	NB	84	18
2	11.8	1.0	8	22.6	75	22.8	2.4 <sup>4)</sup>	26	4	980	81	NB	80	18
3	11.8	1.0	5	2.2	93	22.6	2.7	28	4	1300	99	NB	88	25
4	11.8	1.0	20	2.2	93	22.6	4.1	73	6	2500	132	NB	95	38
5	3.8	6.8	5	22.6	75	22.6	2.6 <sup>4)</sup>	26	5	1450	88	NB	90	18
6	3.8	6.8	20	22.6	75	22.6	2.6 <sup>4)</sup>	26	6	2600	111	NB	95	24
7	3.8	6.8	14	4.2	80	22.7	4.1	54	13	1100	91	NB	83	20

1)室温でのp-キシレン可溶成分量  
2)ポリプロピレン成分の重合割合  
3)分解後の極限粘度  
4)成形後の極限粘度

1)室温でのp-キシレン可溶成分量

2)ポリプロピレン成分の重合割合

3)分解後の極限粘度

4)成形後の極限粘度

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